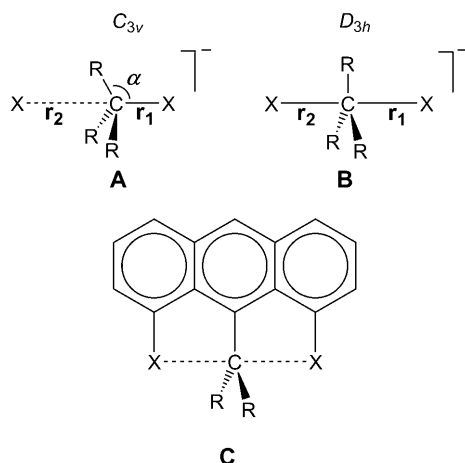


Hypervalent Carbon Atom: “Freezing” the S_N2 Transition State**

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The quest for hypervalent molecules, in particular ones involving pentavalent carbon atoms, has challenged chemists for about a century.^[1] Over the decades, the non-hypervalence (e.g., **A**; r_1 and r_2 are bond distances) or hypervalence (e.g., **B**)



of various atoms in both molecular as well as extended structures has been investigated.^[2,3] Recently, we have addressed the issue of why silicon is hypervalent (i.e., pentavalent) in $[Cl-SiH_3-Cl]^-$, whereas the carbon atom in $[Cl-CH_3-Cl]^-$ is not.^[4] In terms of this ball-in-a-box model, silicon fits perfectly into the box constituted of five substituents. Carbon, in contrast, is too small and, in a sense, “drops to the bottom” of the box leading, consequently, to a Cl^-H_3CCl species having one long C–Cl bond, one localized C–Cl contact, and a pyramidalized CH_3 unit. The validity of this model was extended to heavier central group-14 atoms (Ge, Sn, Pb) as well as to other axial substituents (F).^[4]

Herein, we present computational evidence that, under certain conditions, a carbon atom can become hypervalent as

the central atom in a D_{3h} -symmetric, trigonal-bipyramidal $[X-CR_3-X]^-$ species. This hypervalence comes down to “freezing” the S_N2 transition state,^[5] that is, converting it from a labile first-order saddle point into a stable equilibrium structure. Note, however, that in the present work, at variance with previous reports on hypervalent carbon atoms, the axial substituents are not geometrically confined by a molecular scaffold such as **C**.^[6] Our evidence is based on relativistic density functional theory (DFT) computations with the ADF program at ZORA-OLYP/TZ2P.^[7]

The idea is that if the CR_3 moiety in $[X-CR_3-X]^-$ is sufficiently rigid, the ball-in-a-box model (central atom moving within a box of substituents) will break down and the system rather behaves as one planar CR_3 unit between two X groups (see disk-between-balls model^[8]). The behavior is then identical to that of the isoelectronic (3-center-4-electron) trihalides which form perfectly hypervalent, $D_{\infty h}$ -symmetric $[X-Y-X]^-$ structures.^[4,9] We have previously found such behavior for the noble gas (Ng)-methyl cation complexes $[Ng-CH_3-Ng]^+$ (with Ng = He, Ne), which are isoelectronic with $[Cl-CH_3-Cl]^-$ but, at variance to the latter, adopt perfectly hypervalent equilibrium structures **B**.^[8,10]

The question now is: can we extend the behavior of CR_3 , which serves as a rigid disk between two axial substituents in the weakly bound noble gas complexes, to the anionic $[X-CR_3-X]^-$ species which feature significantly more stable axial bonds. The answer turns out to be yes. An interesting first indication for this was that by making CH_3 rigid in an artificial manner, $[Cl-CH_3-Cl]^-$ became hypervalent. Therefore, by freezing the CH_3 umbrella motion (by keeping only α fixed at 90° ; see **A**), the imaginary frequency of $i337\text{ cm}^{-1}$, associated with an asymmetric Cl–C–Cl stretch vibration, becomes positive. In other words, the C–Cl bonds in $[Cl-CH_3-Cl]^-$ lose their tendency to localize.

Next, we undertook a quest for CR_3 radicals ($CR_3^\cdot$) which naturally show an increased resistance against pyramidalization as compared to $CH_3^\cdot$. This resistance may be achieved by choosing the substituents R which stabilize the radical electron in the carbon $2p_z$ atomic orbital (AO) on $CR_3^\cdot$ through π -acceptor orbitals on R (see **D**). This mechanism in favor of keeping a planar $CR_3^\cdot$ arrangement would then be active and even more pronounced in the negatively charged $[X-CR_3-X]^-$ in which the $2p_z$ AO is further populated.^[4] Furthermore, substituents that are more bulky than R = H should also prevent pyramidalization for steric reasons, that is, R–R repulsion.^[11] Nonetheless, we do not strive for bulkiness because in the five-coordinate species such steric factors work against hypervalency.^[4,5e]

Figure 1 shows the energy of various $CR_3^\cdot$ species as a function of the angle θ ($\theta = \alpha - 90^\circ$, see **A**) which measures

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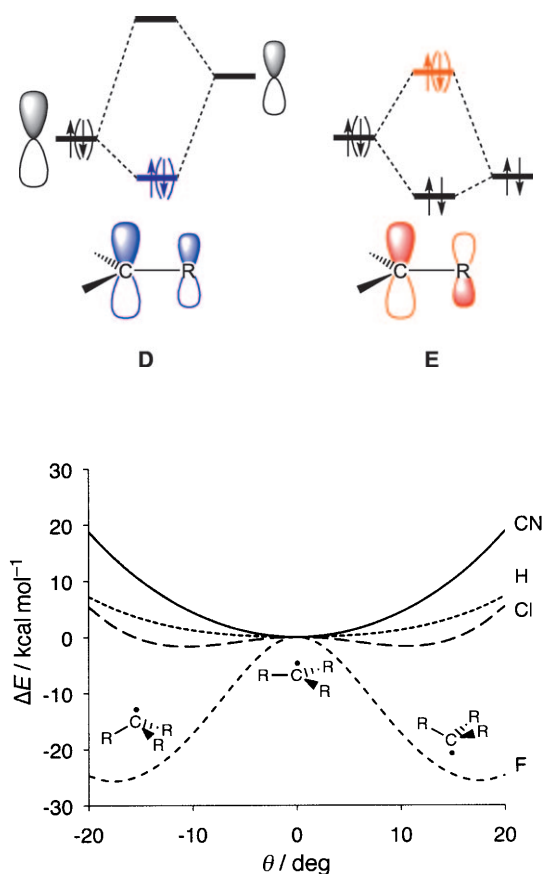


Figure 1. Relative energy, ΔE , of CR_3^- as a function of the distortion angle θ ($\theta = \alpha - 90^\circ$, see A) for $\text{R} = \text{F}$, Cl , H , and CN , computed at ZORA-OLYP/TZ2P.

how far the species deviates from planarity. As can be seen, the extent to which the energy goes up on pyramidalization increases indeed from $\text{R} = \text{H}$ to CN , thus indicating that $\text{R} = \text{CN}$ would be a good candidate for achieving a hypervalent $[\text{X}-\text{CR}_3-\text{X}]^-$ species. To probe this principal, we have also introduced π -donating substituents, $\text{R} = \text{F}$ and Cl , which

destabilize the central $2p_z$ electrons of the carbon atom (see E). As expected, the tendency to pyramidalize increases in the order of $\text{R} = \text{H}$, Cl , and F (see Figure 1).

Finally, we constructed the five-coordinate $[\text{X}-\text{CR}_3-\text{X}]^-$ species using $\text{R} = \text{H}$ as a reference, and the substituent that reinforces the rigidity of CR_3 , namely, $\text{R} = \text{CN}$ (see Table 1). For $\text{R} = \text{H}$, one can recognize that the tendency of $[\text{X}-\text{CR}_3-\text{X}]^-$ to localize the axial bonds decreases together with the decreasing axial $\text{C}-\text{X}$ bond strength in the order of $\text{X} = \text{F}$, Cl , Br , I , and At . In the first place, this is reflected by the decreasing height of the central barrier which goes from approximately 9 to 3.9 kcal mol^{-1} . But it also shows up in the systematic weakening of the negative force constant k^{umbrella} of the umbrella mode within this series, from -0.0906 to -0.0437 a.u.

This trend within the series of halogens is also reproduced for the substituent $\text{R} = \text{CN}$. Importantly, however, the increasing rigidity of CR_3 from $\text{R} = \text{H}$ to CN additionally reduces the tendency of $[\text{X}-\text{CR}_3-\text{X}]^-$ to localize the axial bonds. For $\text{X} = \text{Br}$ and $\text{R} = \text{CN}$, the D_{3h} -symmetric five-coordinate species $[\text{X}-\text{CR}_3-\text{X}]^-$ is only 0.04 kcal mol^{-1} above the localized C_{3v} -symmetric equilibrium structure $\text{X}^- - \text{CR}_3\text{X}$. Note that although the force constant k^{umbrella} of $[\text{Br}-\text{C}(\text{CN})_3-\text{Br}]^-$ is still negative (i.e., the species is still labile with respect to $\text{C}-\text{X}$ bond localization), it has dropped in absolute terms to the relatively small value of -0.0047 a.u. This value is more than an order of magnitude smaller than the k^{umbrella} of $[\text{Br}-\text{CH}_3-\text{Br}]^-$ which amounts to -0.0571 a.u.

Indeed, as we proceed in this manner, we eventually arrive at a viable hypervalent carbon species $[\text{X}-\text{CR}_3-\text{X}]^-$ where $\text{X} = \text{I}$ as well as At and $\text{R} = \text{CN}$. Thus, $[\text{I}-\text{C}(\text{CN})_3-\text{I}]^-$ and $[\text{At}-\text{C}(\text{CN})_3-\text{At}]^-$ are D_{3h} -symmetric, pentavalent equilibrium structures with positive force constants, k^{umbrella} , of 0.0024 and 0.0026 a.u., respectively. The species $[\text{I}-\text{C}(\text{CN})_3-\text{I}]^-$ and $[\text{At}-\text{C}(\text{CN})_3-\text{At}]^-$ were confirmed as stable pentavalent equilibrium structures, even on the zero-point vibrational energy (ΔZPE) corrected potential energy surface (Table 1).^[12] Note that the inclusion of ΔZPE corrections also converts $[\text{Br}-\text{C}(\text{CN})_3-\text{Br}]^-$ effectively into a stable pentavalent species.

Table 1: Valence of the central carbon atom in $[\text{X}-\text{CR}_3-\text{X}]^-$.^[a]

$[\text{X}-\text{CR}_3-\text{X}]^-$ R	X	Rigidity of CR_3 ^[b] k^{umbrella} [a.u.]	$\text{C}-\text{X}^{\text{ax}}$ [kcal mol^{-1}]	$ r_1 - r_2 $ [Å] ^[c]	Complex [kcal mol^{-1}] ^[d]	Barrier [kcal mol^{-1}] ^[e]	Barrier + ΔZPE [kcal mol^{-1}] ^[f]	C Valency
H	F	-0.0906	-45.0	1.25	-15.7	8.03	7.71	non-hypervalent
H	Cl	-0.0717	-31.8	1.55	-9.0	8.77	8.23	non-hypervalent
H	Br	-0.0571	-28.7	1.55	-8.0	6.30	5.78	non-hypervalent
H	I	-0.0501	-25.4	1.53	-7.3	5.34	4.82	non-hypervalent
H	At	-0.0437	-23.7	1.44	-6.6	3.90	3.40	non-hypervalent
CN	F	-0.0537	-83.5	0.69	-53.8	4.26	3.83	non-hypervalent
CN	Cl	-0.0197	-53.3	0.75	-25.5	1.00	0.76	non-hypervalent
CN	Br	-0.0047	-47.9	0.44	-22.8	0.04	0.00	hypervalent
CN	I	0.0024	-43.1	0.00	-21.0	0.00	0.00	hypervalent
CN	At	0.0026	-41.9	0.00	-21.2	0.00	0.00	hypervalent

[a] Computed at ZORA-OLYP/TZ2P. [b] Force constants of umbrella mode k^{umbrella} and heterolytic $\text{C}-\text{X}^{\text{ax}}$ interaction energies, ΔE_{int} , between the corresponding molecular fragments frozen to the geometry they adopt in the overall D_{3h} -symmetric species. [c] Difference in axial bond distances in equilibrium structure. [d] Complexation energy of $\text{X}^- + \text{CR}_3\text{X}$. [e] Central S_N2 energy barrier. [f] Central S_N2 energy barrier with zero-point vibrational energy correction.

The results are relatively robust with respect to variations in the methodology which we have explored by further increasing the basis-set flexibility and polarization (using ZORA-OLYP/QZ4P), and replacing the OLYP approach by density functionals that, in general, yield somewhat higher barriers (using ZORA-OPBE/TZ2P and ZORA-M06/TZ2P; see the Supporting Information).^[7] All these approaches consistently confirm the decrease of the central S_N2 barrier and the shift of the force constant k^{umbrella} towards the positive domain, as one goes from $R=H$ to CN (quite pronounced effect) and as X varies along F, Cl, Br, I , and At (smaller steps). The exact point at which hypervalence is achieved varies somewhat with the approach. On the ZPE-corrected potential energy surface, ZORA-OLYP/TZ2P yields hypervalence for $[Br-C(CN)_3-Br]^-$, whereas ZORA-OLYP/QZ4P and ZORA-OPBE/TZ2P arrive at hypervalence starting from $[I-C(CN)_3-I]^-$. However, $[At-C(CN)_3-At]^-$ is hypervalent at all levels of theory, including ZORA-M06/TZ2P. Our proof of principal may inspire the quest for hypervalent carbon in trigonal bipyramidal configurations.

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